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PROGRESS REPORT #1
Contract N00014-92-C-0172
May 1993

Single Crystal Diamond Thin Films

EPION CORPORATION

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13. ABSTRACT *(Maximum 200 words)*

One possibility for accomplishing growth of single crystal diamond film on a nondiamond substrate is based upon ion implantation of carbon atoms into crystalline copper. In spite of widespread interest in the concept, heteroepitaxial diamond growth by this approach has never been confirmed. The objective of this program is to develop specialized ion implantation capabilities for C^+ into Cu processing under conditions for which heteroepitaxial formation of diamond on copper may be feasible. A 200 keV medium current ion implantation system has beer modified to allow implantations to be performed into substrates at temperatures up to 1000°C, to incorporate background atomic hydrogen in the vicinity of the substrate surface during implantation, and to facilitate in-situ CVD diamond growth processing. Apparatus development has been completed and process investigations have been initiated.

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Bedford, MA 01730

Period Covered: 28 July 1992 - 27 April 1993

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I. INTRODUCTION

This Progress Report #1 describes activities under SBIR Phase II Contract N00014-92-C-0172 "Single Crystal Diamond Thin Films" during the period 28 July 1992 through 27 April 1993. The intent of this program is to conduct C^+ implantation into copper under conditions for which heteroepitaxial formation of diamond upon copper may be feasible. Efforts during the period of this report have emphasized development of unique ion implantation apparatus and associated procedures which are to be required.

The C^+ implantation into Cu approach to heteroepitaxial formation of diamond was suggested by J. Prins in 1990[1]. Cu has a lattice similar to that of diamond and does not form a carbide. Carbon atoms can be introduced into the vicinity of a copper surface by means of ion implantation. At sufficiently high temperature, implanted C atoms should be free to diffuse to the copper surface where they will combine under the influence of short range forces of the Cu lattice. The cubic crystal structure of copper with 3.6151Å lattice parameter is sufficiently similar to that of diamond with 3.5667Å lattice parameter that it may serve to encourage bonding of the carbon into diamond coordinated with the copper host.

C^+ into Cu investigations to date have produced only a few encouraging observations[2,3] among mainly negative results[4,5,6,7]. In

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1 J.H.Prins and H.L.Gaigher, "A TEM Study of Layers Grown on Copper using Carbon Ion Implantation", p561, MRS Proceedings of 2nd International Conference on New Diamond Science and Technology, Washington (1990)

2 J.Narayan, V.P.Godbole and C.W.White, "Laser Method for Synthesis and Processing of Continuous Diamond Films on Nondiamond Substrates", Science **252**, 416 (1991)

3 H.A.Hoff, D.J.Vestyck, J.E.Butler and J.F.Prins, Ion Implanted, Outdiffusion produced Diamond Thin Films", Appl. Phys. Lett. **62** (1), 34 (1993)

4 S.-T.Lee, S.Chen, G.Braunstein, X.Feng, I.Bello and W.M.Lau, "Heteroepitaxy of Carbon on Copper by High Temperature Ion Implantation", Appl. Phys. Lett. **59** (7), 785 (1991)

5 T.P.Ong, F.Xiong, R.P.H.Chang and C.W.White, "Mechanism for Diamond Nucleation and Growth on Single Crystal Copper Surfaces Implanted with Carbon", Appl. Phys. Lett. **60** (17), 2083 (1992)

6 S.-T. Lee, S.Chen, J.Agostinelli, G.Braunstein, L.J.Huang and W.M.Lau, "Laser Processing of Carbon-Implanted Cu, Ni, and Co Crystals: An Attempt to Grow Diamond Films", Appl. Phys. Lett. **60** (18), 2213 (1992)

most investigations, carbon layers formed as a result of C^+ implantation into Cu at high temperature have been crystalline graphite with c-axis oriented normal to the copper surface[4,5]. No systematic orientation relative to the copper lattice has yet been reported.

The premise of the present investigation is that, if the concept suggested by Prins is to succeed, the processing will have to be conducted under conditions quite different from those employed in other investigations. It is believed that limitations of conventional ion implantation equipment, in combination with experimental conditions selected so as to result in carbon layers sufficiently thick to be characterized directly, may have compromised experimental studies to date. The objective of this program is to develop and evaluate modified implantation capabilities for C^+ into Cu processing under conditions which should not be detrimental to heteroepitaxial diamond growth. Requirements are believed to include:

- C^+ implantation should be conducted at temperature sufficiently high that implanted C is free to migrate within the Cu during the implant
- C^+ implantation rate should be sufficiently low as to allow adequate time for migration of the C during the implant
- conditions should be established in the vicinity of the Cu surface to favor creation of diamond and to suppress formation of graphite
- the amount of implanted C should be reduced to the minimum required to form a few monolayers of diamond upon the copper surface; diamond mass should be built up upon this nucleation layer by an auxiliary CVD operation.

All program activity through the period of this report has been for the purpose of developing new ion implantation techniques able to satisfy the requirements above as a minimum. By the end of the period, a series of experiments was in progress to determine whether the modified ion implantation techniques will provide ability to influence and control process results.

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7 Z.H.Zhang, L.Chow, K.Paschke, N.Yu, Y.K.Tao, K.Matsuishi, R.L.Meng, P.Hor and W.K.Chu, "High Energy Carbon Ions Implantation: An Attempt to Grow Diamond Inside Copper", Appl. Phys. Lett. **61** (22), 2650 (1992)

II. PROGRAM STATUS

II.1 Ion Implantation Apparatus and Technique Development

Program efforts during the period covered by this report have been primarily apparatus and technique development. Ion implantation systems developed for semiconductor device production do not support implantation into very high temperature (>800°C) substrates and do not facilitate in-situ auxiliary CVD processing as part of their operations. These capabilities are considered essential to this program. The modifications required to conventional ion implantation equipment are substantial and cannot be made without adversely affecting ability of the equipment to perform operations for which it was originally designed.

It was recognized prior to program inception that alterations which should be made to an ion implantation system in order to perform this program are such that restoration of the equipment to its original operating configuration for normal use would be a rather major task. To perform planned investigations on an occasional use basis by employing borrowed or rented implantation equipment, to be restored after each use, would be impractical and would unacceptably restrict the nature of the adaptations which could be made. Consequently, in preparation for this work, Epion made capital equipment purchase of a used Varian Model DF4 200 keV medium current ion implanter which has now been dedicated to the program. Program activities during the period of this report have involved design, installation and test of modifications to this ion implanter and development of procedures for its use to investigate heteroepitaxial formation of diamond by C^+ into Cu processes. Modifications to the ion implantation system have included:

- removal of the cassette-to-cassette wafer handling apparatus, the wafer transport vacuum locks and the wafer implant platen; revision of the system controls to allow operation without these components

- addition of a separately pumped experimental process chamber and sample entry vacuum lock onto the existing end station.

- introduction of a substrate carrier stage into a cylindrical tube furnace designed to allow implantations at temperatures up to 1000°C without ion beam heating assistance

- addition of hot filament and CH_4/H_2 gas introduction capabilities into the substrate furnace to allow in-situ CVD diamond growth processing

- revision of the implantation system ion optics to allow control and measurement of ion beams directed onto hot, gas-enveloped, electron-flooded substrates

- introduction of ability to perform narrow line beam ion implantation with controlled translation of the line beam across the substrate in process.

Figure 1 shows original configuration of the Varian Model DF4/3000 ion implantation system. Ions are created by a hot cathode arc discharge within a gas fed ion source, extracted at 25 kV for mass analysis using an adjustable electromagnetic field, accelerated up to as much as 200 kV, then electrostatically scanned over the individual substrate being processed. Usable beam current is approximately 1 milliampere maximum, generally much less for ions generated from compound gases which produce a distribution of various mass species. Ion dose is determined by direct integration of charge collected by the substrate holder. Dose uniformity, accuracy and reproducibility are typically of the order of ±1%.

In order to employ high substrate temperatures, background gas environments and auxiliary processing during and following C^+ implants into Cu sheet substrates, the production end station of the DF4/3000 implanter was removed and replaced by the apparatus shown in the photographs of Figure 2 and Figure 3. The apparatus includes:

- a high vacuum process chamber
- a high temperature vacuum furnace
- an assembly of monitor electrodes, beam slits, process filament and gas nozzle within the vacuum furnace
- a vacuum lock assembly with magnetically coupled sample transport
- stepper motor control over sample vertical position.

The schematic diagram of Figure 4 indicates the relationship of the experimental process apparatus to the remaining structure of the original implanter.

An existing water-cooled stainless steel box chamber has been employed as the process chamber. The chamber is connected to a high speed 6-inch diffusion pump/gate valve/liquid nitrogen trap combination capable of reducing the chamber pressure to below 1×10^{-6} Torr. A gate valve to the implanter beamline allows the process chamber to be isolated for performance of post-implant in-situ CVD diamond growth at backfill pressures of the order of 50 Torr.

The sample furnace employs a 4.5 inch diameter by 7 inch long slotted cylindrical graphite heater element driven by an SCR controller operating through a step-down transformer. The heater element is surrounded by rigid graphite felt insulation and is lined by a quartz tube sample enclosure. A thermocouple in contact with the quartz liner is used for temperature control feedback to the SCR power controller. Approximately 2 kW is required to maintain 1000°C furnace temperature. With the furnace at 1000°C, process chamber pressure remains below 1×10^{-6} Torr.

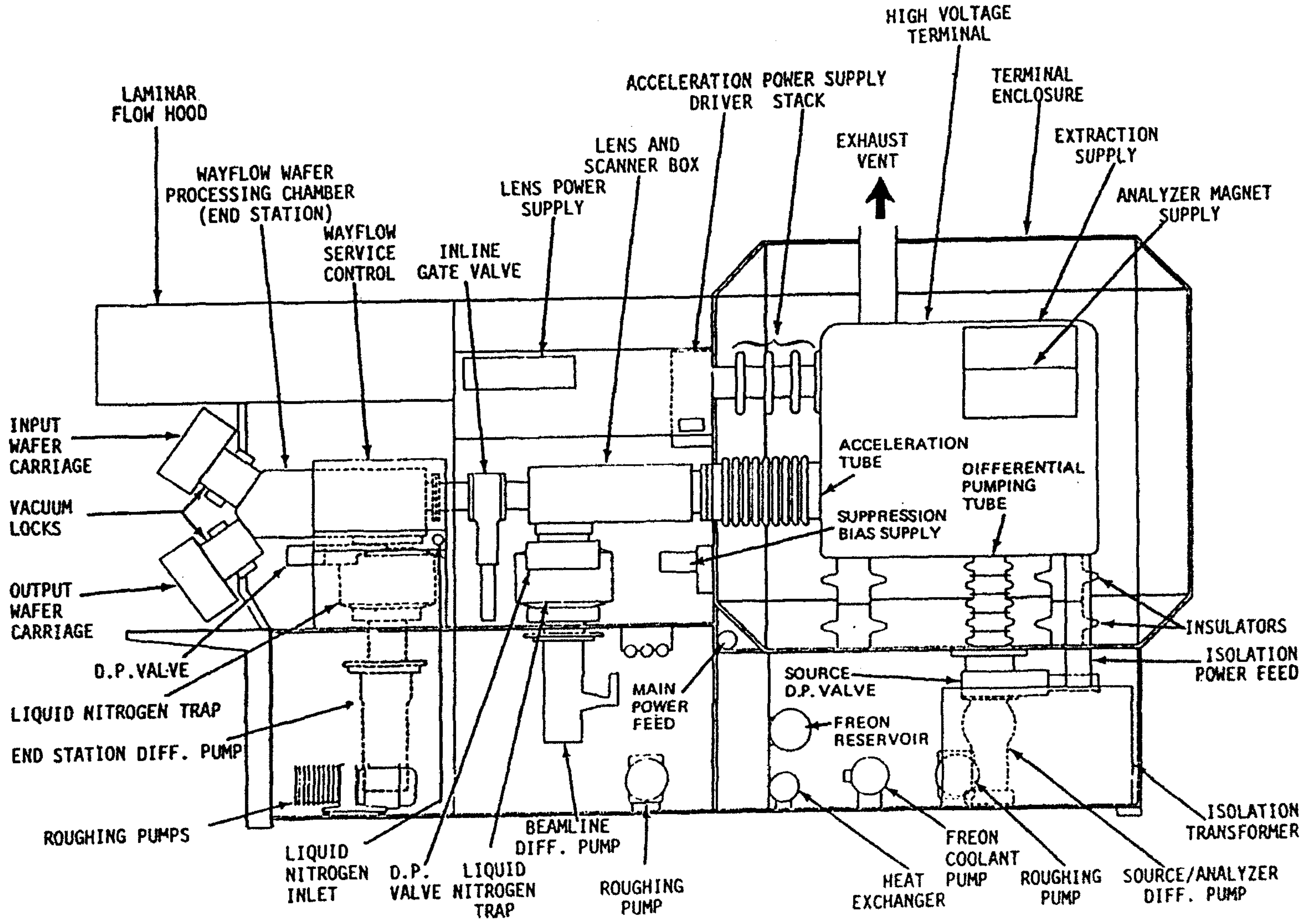

Figure 1
Configuration of DF4/3000 Ion Implantation System

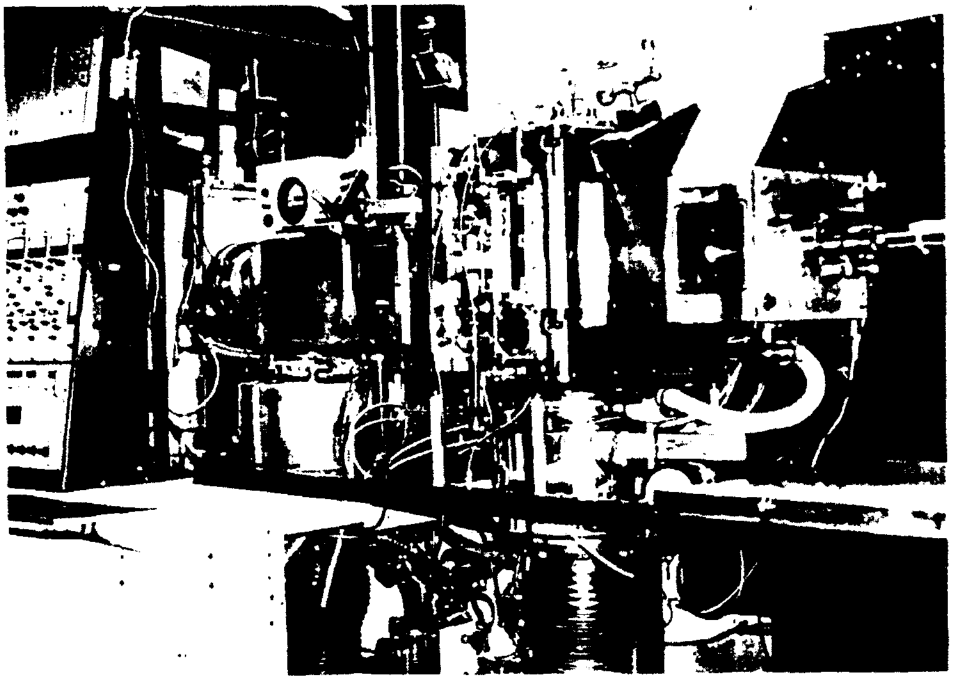

Figure 2
Process Apparatus attached to Implanter

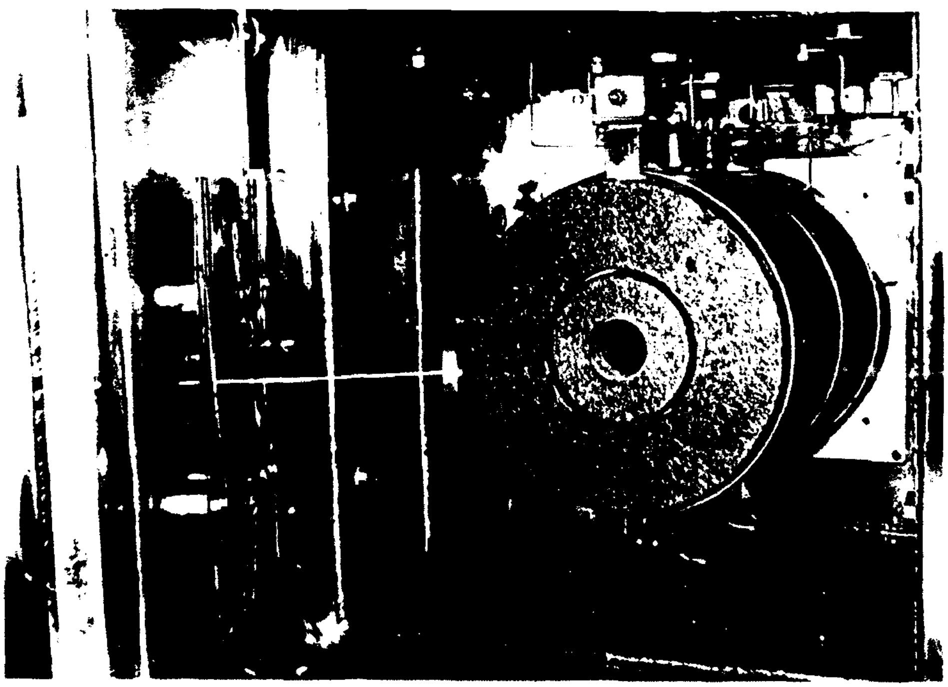

Figure 3
Vacuum Furnace for High Temperature Implantations

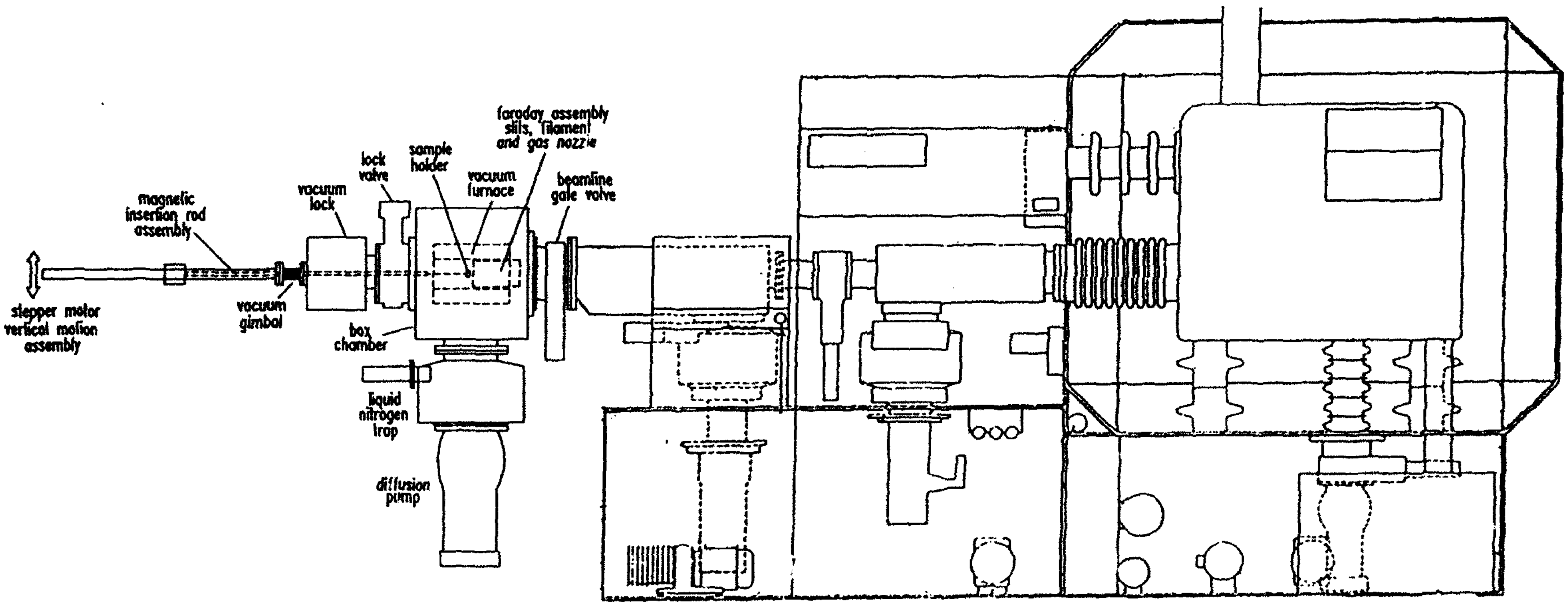

Figure 4
Configuration of Modified Implantation Apparatus

A schematic of the substrate process zone within the tube furnace is shown in Figure 5. The ion beam enters one end of the furnace through a graphite aperture plate and a series of stainless steel heat shields, then passes through a pair of cylindrical graphite electrodes which serve in conjunction with the sample holder as a Faraday collector beam current monitor. Substrates are introduced through the opposite end of the furnace on the end of a magnetically coupled transport rod assembly. A tungsten filament and a small nozzle for introduction of H_2 and CH_4 gases are positioned close to the substrate face location. For investigation of travelling line beam C^+ implantation effects, a graphite slit can be mounted in the end of the graphite cylinder next to the sample holder. The sample itself can be moved vertically past the beam slit at rates as low as 0.2 μm/sec or as high as hundreds of μm/sec by stepper motor controlled elevation of the back end of the insertion rod assembly.

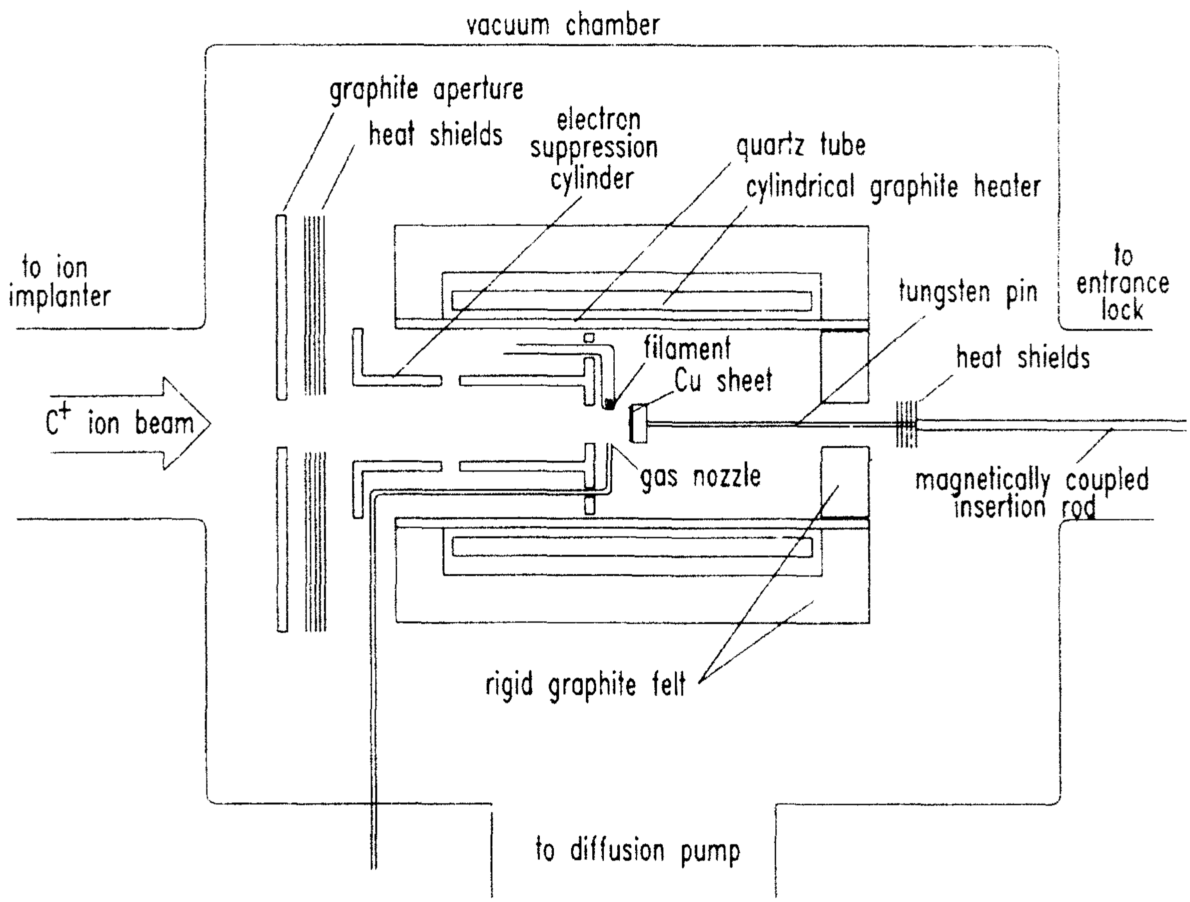

Figure 5
Process Fixturing for C^+ into Cu Studies

It has been observed that beam current measurements made by collection of charge carried to the substrate being processed can become unreliable when the substrate is at very high temperature and/or is being bombarded by electrons from a nearby filament. A second ion beam monitor positioned outside the sample furnace and shielded from the substrate filament is used to maintain ion dose accuracy under these conditions. This remote monitor consists of a graphite annulus which samples the ion beam passing through it to reach the substrate in process.

II.2 Implantation Studies

By the end of the period of this report, the modified implantation apparatus had been made fully operational and experimental implantation studies into copper had been initiated. Experimental substrates are disks cut from high purity polycrystalline copper sheet or from a single crystal copper ingot. Substrates are inserted through the vacuum lock into the end station furnace and then elevated to selected temperature prior to implant initiation. Upon completion of implantation, and any subsequent in-situ treatments, substrates are withdrawn into the vacuum lock to cool to room temperature before removal to atmosphere. Process times for individual samples have ranged from 2 to 10 hours.

After implant, samples have been examined under an optical microscope and by SEM. Part of each sample has been subjected to a short diamond growth operation in a filament-assisted CVD reactor which is not part of the implantation apparatus. Each sample has then been reexamined by microscope and SEM. Portions of selected samples have been transferred to the University of Houston for other examinations, including Raman spectroscopy analysis.

The purpose of ten initial C^+ implantation experiments completed through April has been to survey the influence of the process variations which are now available. It has been found that the new implantation tools add complexity to an already complex situation occurring on the implanted copper. Many new effects are found on copper subjected to modified implantation procedures. It has been observed that the following parameters have ability to cause major alteration to the character of the implanted copper surface:

- temperature during implant/after implant
- presence of a hot filament with H_2 gas background
- proximity to the filament
- ion species employed (C^+, CO^+, etc.)

A broad range of variations in morphology of the copper surface, local structure associated with segregation of the carbon from the copper, formation of a surface carbon layer, the nature of the carbon layer, density of diamond nucleation which will occur during CVD growth, etc., are caused by adjustment of the parameters listed above. Due to the complex nature of the effects which are being

produced, Epion prefers to accumulate additional information before attempting to present or explain any of the results. To date there has been no evidence of heteroepitaxial nucleation or of diamond formation due to carbon implantation. CVD growth of diamond onto implanted copper surfaces has in every instance resulted in individual diamond crystals with no identifiable orientational relationship to the structure of the copper below. Whether this must continue to be the case should be determined from investigations to be performed during the next three months.

II.3 Analytical Studies

A subcontract has been awarded to the Texas Center for Superconductivity at the University of Houston for conduct of analytical evaluations in support of C^+ into Cu process development. The objective of the work being performed is to provide assistance in the identification of processing conditions which will facilitate formation of heteroepitaxial nucleation interfaces for diamond growth on crystalline copper substrates. Professor Wei-Kan Chu, Deputy Director of the Center for Superconductivity is the Principal Investigator for the subcontract studies. Dr. Zuhua Zhang is the scientist directly responsible for most of the experimental work being performed. The subcontract analytical investigations were initiated in late January 1993.

In addition to providing evaluations of samples produced at Epion, studies being performed at the University of Houston involve examination of specific technical issues associated with the C^+ into Cu concept. Topics include the mechanism by which implanted carbon is able to migrate to the copper surface and the influence of sublimation of copper from the surface upon carbon layer formation.

III. SUMMARY

Ion implantation apparatus has been developed to allow C^+ into Cu processing under conditions not previously available. This apparatus facilitates substrate temperatures up to 1000°C during implantation, provides a method to suppress graphite formation on a copper surface during C^+ implant, offers capability to perform travelling beam implants, and allows in-situ diamond CVD growth processing.

Initial C^+ into Cu investigations have shown that the process results can be very strongly influenced by the implantation variations now available, but no evidence of heteroepitaxial nucleation of diamond has yet been observed. CVD growth onto implanted Cu surfaces has continued to result in formation of nonoriented diamond crystals. Investigations are now directed to evaluation of prospects for achieving heteroepitaxial nucleation.